

Mechanistic Modeling Framework for Predicting Extreme Battery Response: Coupled Hierarchical Models for Thermal, Mechanical, Electrical and (Electro)chemical Processes

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Project # ES198

Timeline

- Project start: 9/22/13
- Project end: 1/10/15
- Percent complete: 20% spent, 25% duration

Budget

- Total project funding
 - DOE share: \$1500K
 - No cost share
- Funded 9/21/13 for FY14-15: \$1500K
- No prior year funding.

Barriers

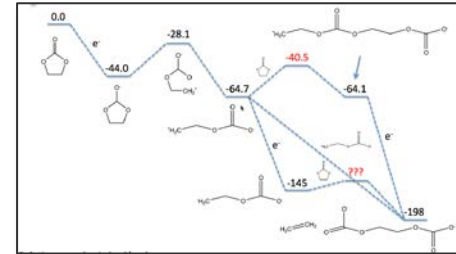
- Abuse tolerance and associated safety concerns is serious public acceptance issue.
- Lack of predictive battery design models with infrastructure for general chemistry and phase change modeling.

Partners

- Sandia National Laboratories (lead)
 - Electrochemical and thermal modeling
- Oak Ridge National Laboratory
 - CAEBAT open architecture integration
- Colorado School of Mines
 - Upscaling of pore-level models

Relevance/Objectives

- Objectives: : The goal is to address root cause and implications of thermal runaway of Li-ion batteries by delivering a software architecture solution that can lead to the development of predictive mechanisms.
 - Incorporate thermo, transport, kinetic properties from literature.
 - Karthikeyan, Sikha, While, *J. Power Sources* 185(2008) 1398-1407: Redlich-Kister, van Laar or Margules parameters for LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, hard carbon, MCMB (Used in later results).
 - Flexibility to incorporate new knowledge/research results.
 - In past three issues of *J. Electrochem. Soc.* (vol. 161, Issues 6-8) there is more than half a dozen examples *each* of thermodynamic, transport and kinetic data or parameters. How do you implement new parameters monthly to keep up?
 - Initial focus on integration of Cantera-based framework for cell-level chemistry/transport into ORNL CAEBAT architecture.



Key Objectives:

- Port 1DElectrode models (C++ Modular Object oriented) from Sandia's Thermal Battery program to the CAEBAT architecture.
- Develop consistent thermodynamic/transport models of the entire cell using CANTERA an open source constitutive modeling package
- Add partial saturation and solid mechanics models to CAEBAT to model gasification and stress-induced degradation phenomena
- Build SEI Models that can predict the autocatalytic temperature behavior experimentally observed
- Upscale microstructure calculations to the macrohomogeneous scale using both averaged results and statistical distributions.
- Develop new models for thermal runaway processes within Li-ion batteries that are based on consistent thermodynamics models.
- Develop a collaborative research program by publishing as open source, and invite other research groups to participate (<http://github.com/cantrilbat>)

Milestones

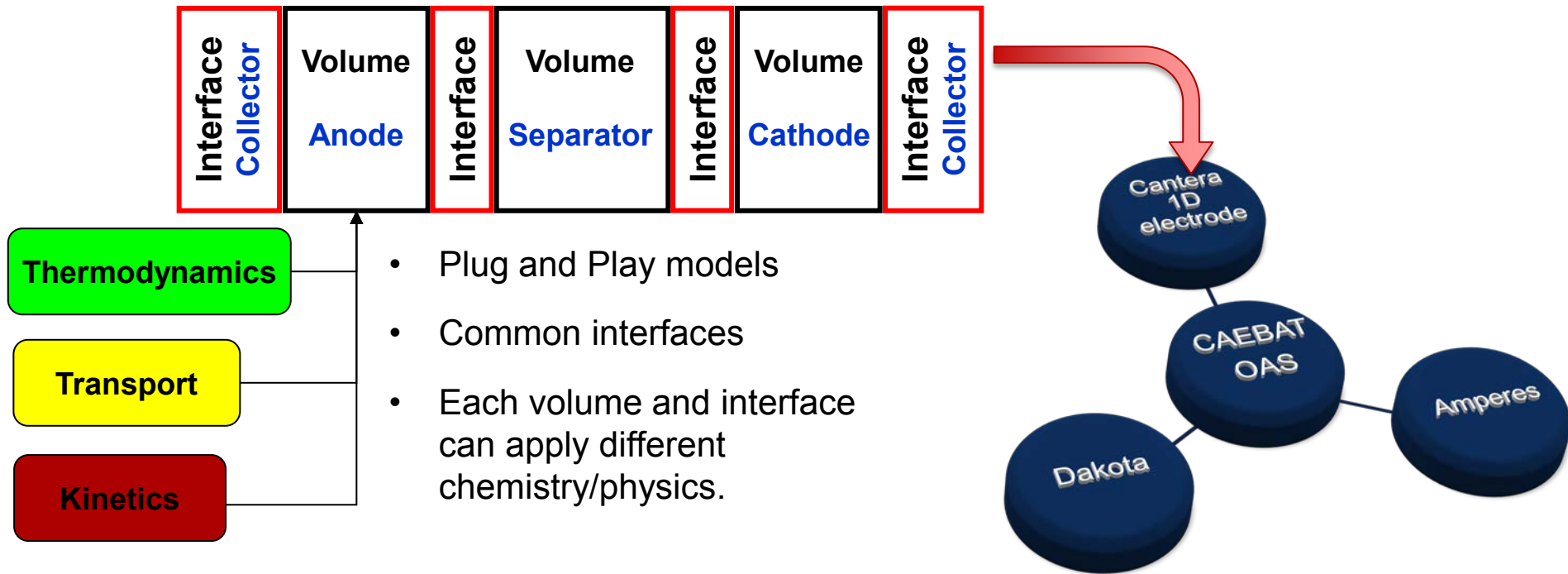
MARK COMPLETE / STATUS AS APPROPRIATE

Date	Milestone
4/1/14	Document progress on how coupling between 1DElectrode object and battery scale within CAEBAT modeling is to be carried out. Document I/O and restart strategy for integrating 1DElectrode within CAEBAT. (Complete)
10/1/14	Verification studies on electrode implementation: comparison against previously implemented models not in Electrode structure.
10/1/14	Implement models for partially saturated porous flow within the CAEBAT/Electrode architecture.
10/1/14	Implement plan for upscaling particle-scale calculations for bulk quantities.
10/1/14	Go/No-go decision: Duplicate existing capability using the NTG and Dualfoil program using the 1DElectrode infrastructure within CAEBAT. A verification exercise will be carried out to demonstrate this basic milestone.
4/1/15	Implement solid mechanics modeling within the CAEBAT/Electrode architecture.
4/1/15	Document upscaling work and publish.
4/1/15	Integrate models for SEI solubility in electrolyte. Demonstrate SEI loss or thinning as a function of the temperature.
10/1/15	Verify solid mechanics modeling within the CAEBAT/Electrode architecture.
10/1/15	Demonstrate qualitative agreement of thermal runaway models against BATLab data.
10/1/15	Exercise battery level modeling to develop examples of thermal-runaway calculations as a function of input parameters.

Approach/Strategy

Approach

- Cantera: open-source C++ framework providing thermodynamics, transports, kinetics. Modular. Highly extensible.
- Recent Sandia, CSM Cantera development: non-ideal thermo, electrochemistry.
- Recent Sandia applications built on Cantera: subgrid and 1D electrode models.



Oak Ridge CAEBAT open architecture for incorporating multi-physics models.

Approach/Strategy - II

Strategy:

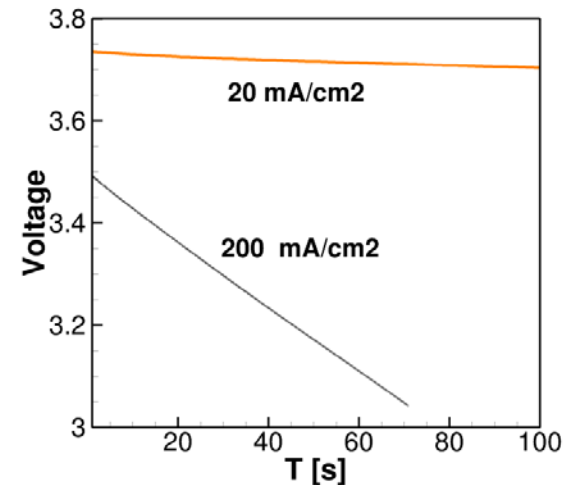
- Incorporate Cantera applications into CAEBAT open architecture.
- Add missing capabilities (side reactions, passivation/SEI layers, gas generation, partially saturated porous flow, solid mechanics)
- Develop upscaling algorithms linking fine-scale to device-scale.
- Demonstrate on thermal abuse scenario.

Milestones

- Partial saturation flow this year
- SEI layer formulations next year

Go/No-Go: (10/1/14)

- Duplicate existing capability (NTG and Dualfoil) with Cantera/1DElectrode within CAEBAT architecture.



Cantera's electrochemistry treatment

Object oriented treatment of homogeneous and heterogeneous phase

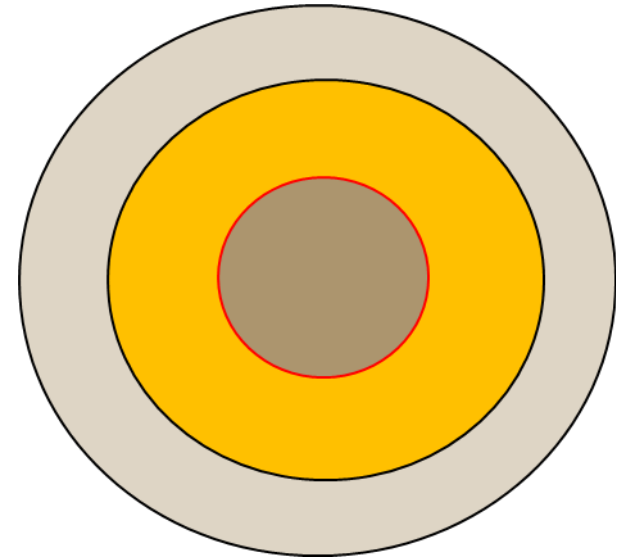
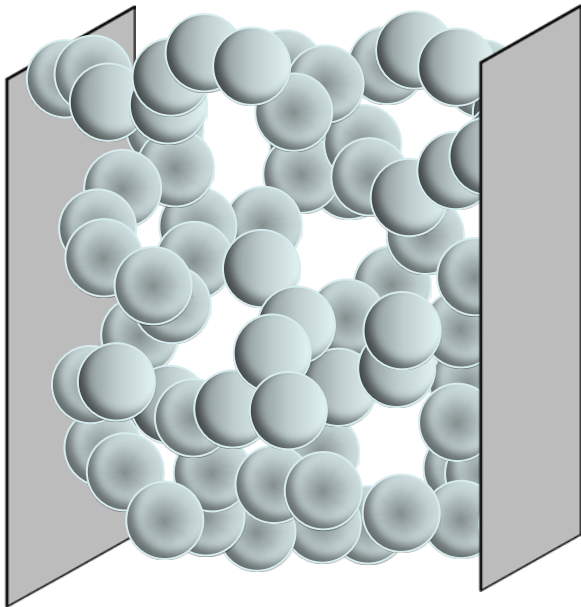
Speciation is treated via a full specification of the chemical potentials of all species including the electron.

Full treatment of Pitzer's brine thermodynamics, molten salt non-ideal thermodynamics, mixtures of organic solvents, etc. Usually, one ionic-species in the mixture must be specified via a convention. Treatment of organic solvents in the works for this project

Electrochemical reactions at interfaces are treated as reversible reactions with potentials modified by the electrochemical potentials of the species – single reaction is compatible with Butler-Volmer formulation, adsorbate-modified behavior can model realistic experiments.

Accomplishments: Electrode Evolution Model

- Finite-capacity porous electrode model:
 - Electrode depletion tracked with representative particle sizes, densities.



- Multiple plateaus can simultaneously react in our implementation of the shrinking core model.
- Reactions at phase interfaces.
- Diffusional losses associated with transport from inner cores.
- Added Radial diffusion electrode objects (TALE method)

Accomplishments – Understanding numerical issues associated
source terms with state variables

Electrode Source term is turned into a time
dependent integral over the time step of the outer loop.

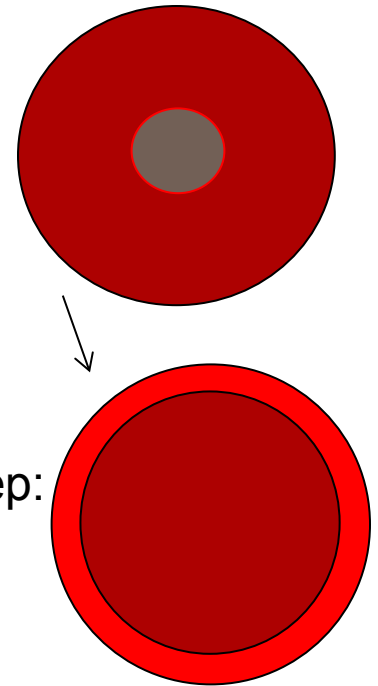
Enables modular software architecture – Already in 3D Code, Aria!

Example – continuity equation for electrolyte species includes a
source term from the electrode reaction,

$$\frac{(V_i C_T \phi X_k)_{n+1} - (V_i C_T \phi X_k)_n}{t_{n+1} - t_n} + n_{iL} \bullet [A_{iL} C_T X_k (\mathbf{v} + \mathbf{V}_k)] + n_{iR} \bullet [A_{iR} C_T X_k (\mathbf{v} + \mathbf{V}_k)] = (V_i w_k)_{n+1}$$

Source term is formally replaced by an integral over the time step:

$$w_{k,n+1}(A_{n+1}, \alpha, t) \rightarrow \frac{\int_{t_n}^{t_{n+1}} w_k(A_{n+1}, \alpha, t) dt}{t_{n+1} - t_n}$$

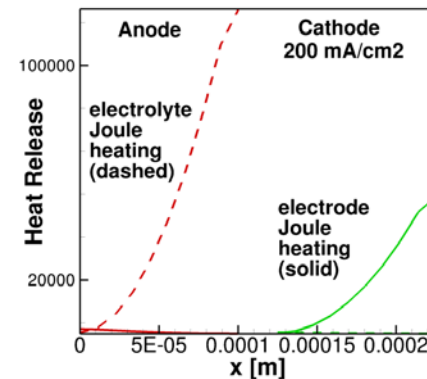
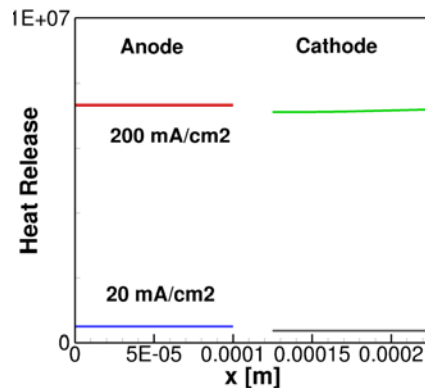


Key to isolating and uncoupling the complexity between 1D and subgrid
models: Requirements: Predictor-corrector time step strategy:

Implicit stiffness coupling still requires jacobian

Accomplishments: Heat Release and

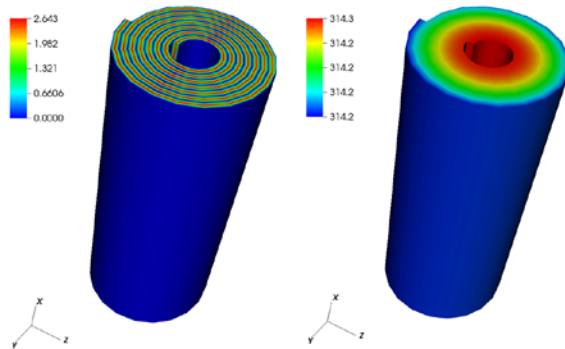
- Added heat release capability to 1DElectrode model as well as upscaling the electrical environment.



- Enthalpy formulation for the energy conservation equation for 1DElectrode under construction.

Essential first task: Incorporate Electrode object into CAEBAT

At the end of the first year we expect to be able to duplicate Dualfoil capability using the 1DElectrode infrastructure within CAEBAT.



Integration issues initially addressed

A verification exercise is being carried out to demonstrate this basic milestone.

Lessons learned, items to be accomplished from dualfoil comparison:

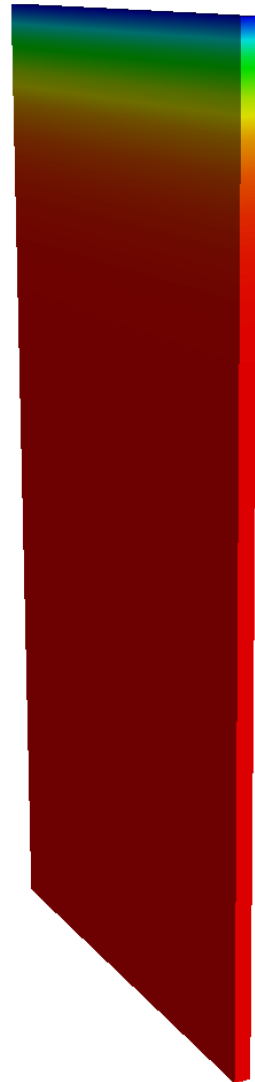
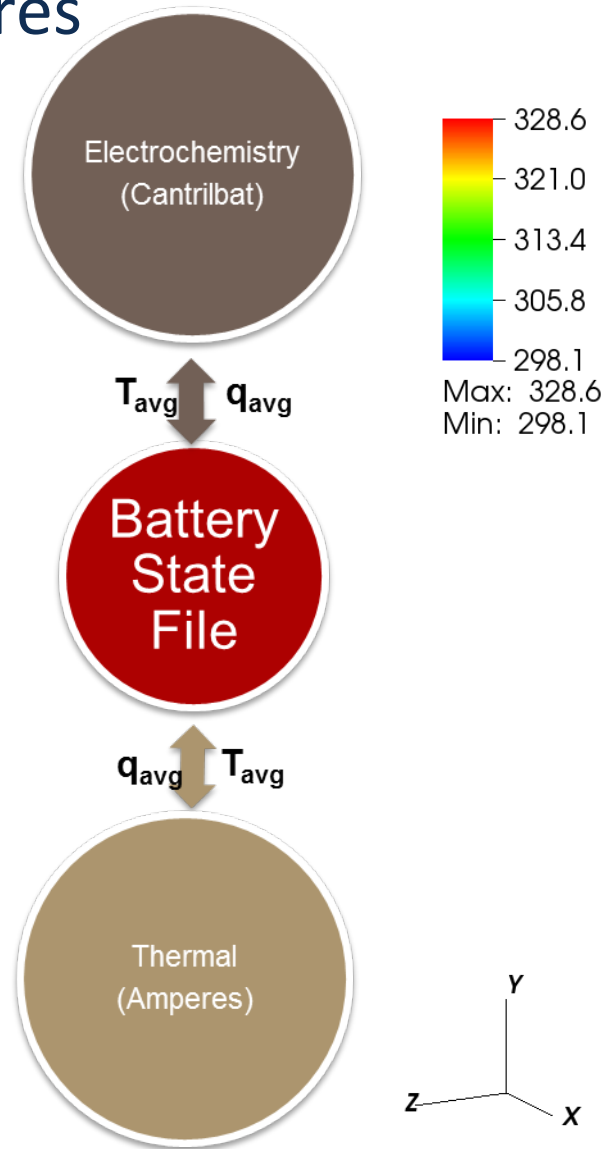
- Include direct parameterization of OCV as an important option in 1DElectrode and Electrode modeling. Note, this is limiting though as it prevents relating molecular structure to OCV through thermo modeling.
- Add empirical but often used exchange current density formulation. Not mass-action based from Marcus theory, but widely used to correlate data
- Either include parameterization for temperature dependence of all thermo parameters and fit to thermo of OCV, or model the temperature dependence of OCV directly

Accomplishments: Cell-level coupling of Cantrilbat

Amperes

Test Case : Unrolled Cell (Electrochemical-Thermal)

- Coarse mesh to model thermal transport over entire domain
- Divide domain into multiple zones
- On each zone run Cantrilbat concurrently at discharge current of 0.3 A/cm^2
- Average zonal quantities of interest transferred through state file.
- Cantrilbat keeps its own more detailed restart file.

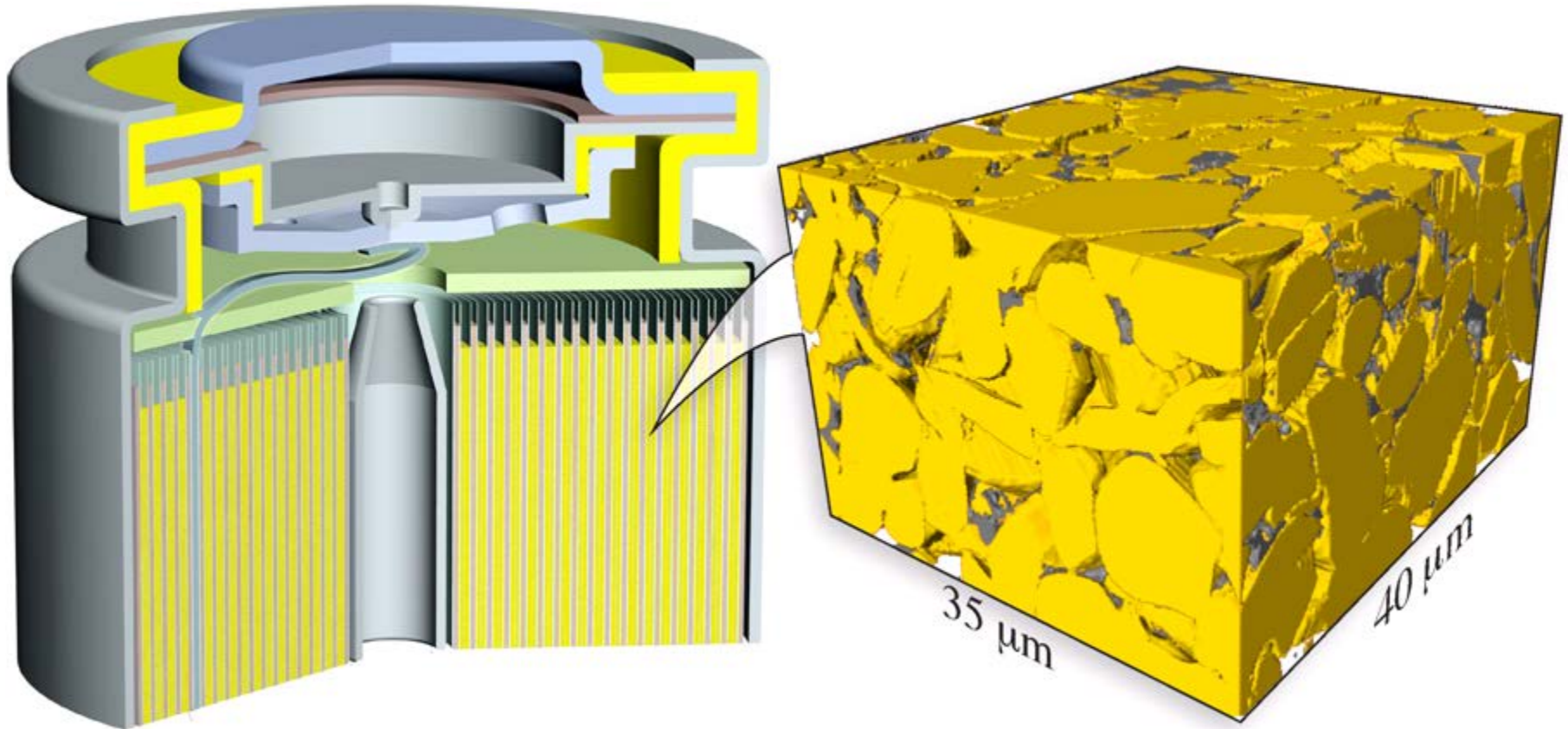


(Not to scale)

Models of realistic electrode microstructures provide information that is unavailable from spherical models

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Actual electrode microstructure is geometrically complex

- Predicting microscale electrochemistry is computationally challenging
- Upscaling is needed understand practical cell performance
- Even at the cell scale, the geometry and materials mix is complex

Actual electrode microstructures can be reconstructed via tomographic interrogation



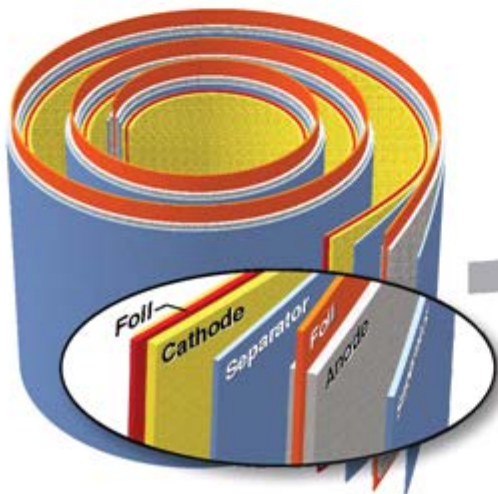
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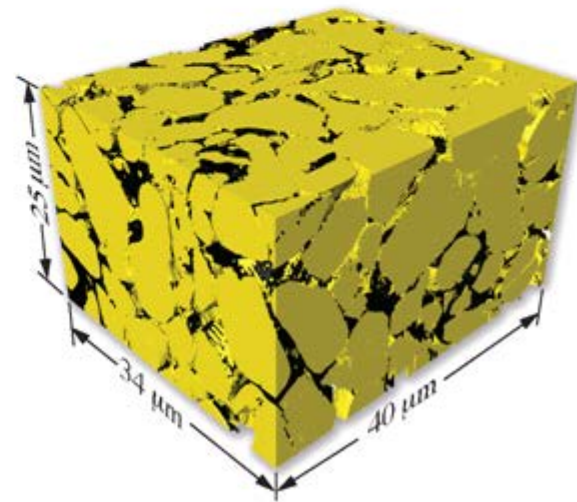
Commercial Li-ion cells

Disassemble



FIB-SEM
electrode images
(typically 200-300)

Software
microstructure
reconstruction

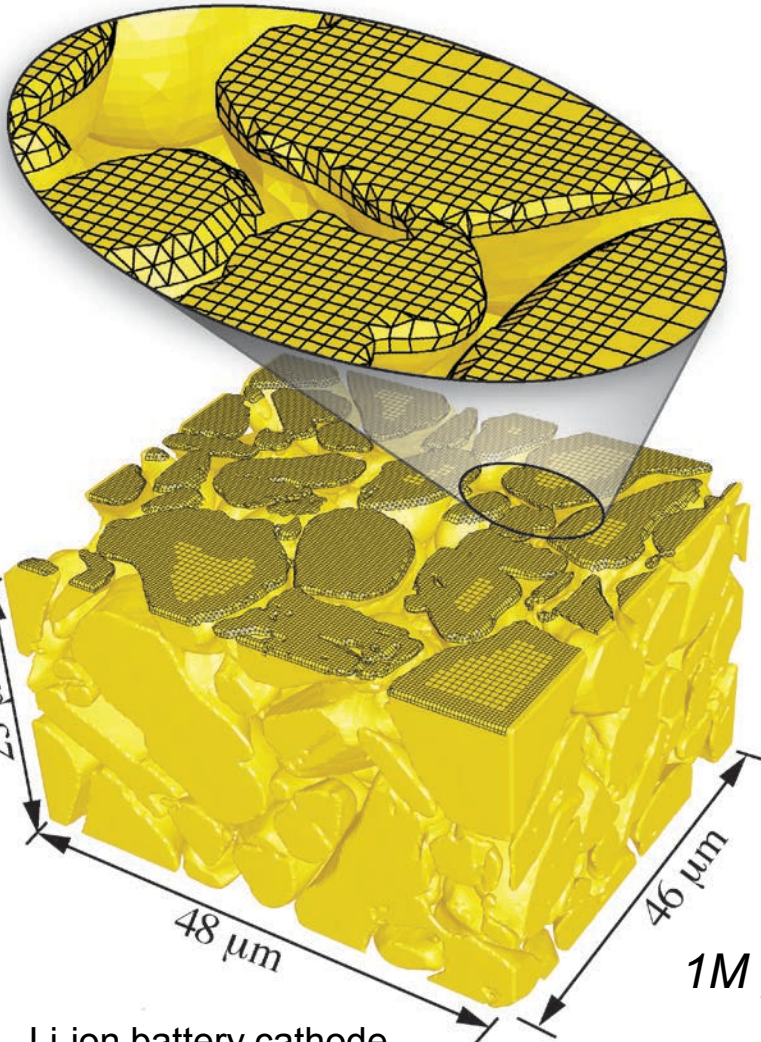


Reconstructed electrode structures are discretized as the basis for detailed computational analysis



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Li-ion battery cathode

Actual 3D geometry is discretized

- Solid phase and pore phase
- We have developed robust algorithms

Model transport and chemistry

- Multicomponent transport in pores
- Heterogeneous catalysis on surfaces
- Electrochemical charge transfer
- Thermal behavior at the microscale

Important questions can be answered

- How does microstructure performance?
- What are the effective properties?
- How does pore space affect ion transport?
- How does microstructure influence heating?

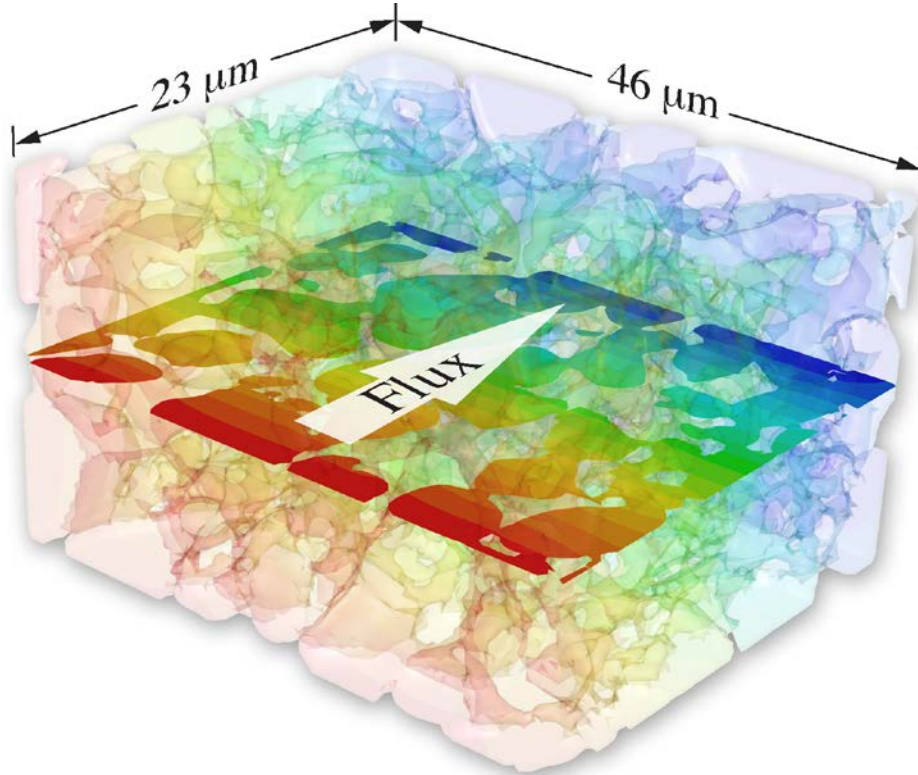
1M polyhedra cells, 4.3M faces, 2.9M nodes

- Wiedemann, et al., *Electrochimica Acta*, 88:580-588 (2013)

Effective properties can be homogenized from microscale electrode simulations

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Simulated transport through a reconstructed composite cathode

Physical properties

- Density and heat capacity
- Volume-weighted average

Conductivity

- Solve heat-conduction problem
- Evaluate heat fluxes
- Derive effective conductivity

Volumetric heat release rate

- Specify temperature
- Specify discharge rate
- Solve electrochemistry problem
- Evaluate local heat release
- Average over microscale sample

The reconstructed electrode samples are small, but representative

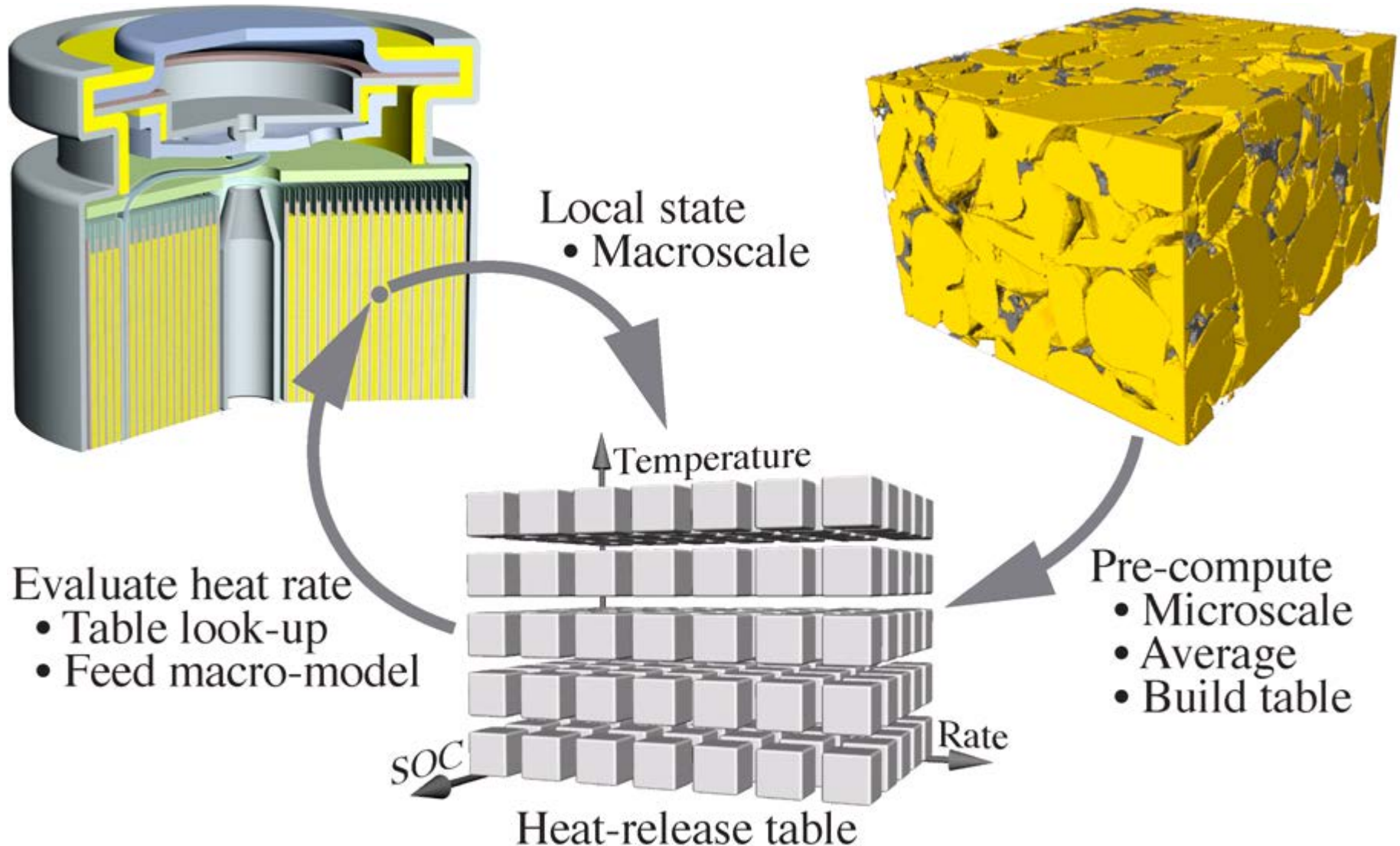
- Millions of finite-volume cells

Pre-computed table look-up may provide a viable route for up-scaling the electrochemical heating



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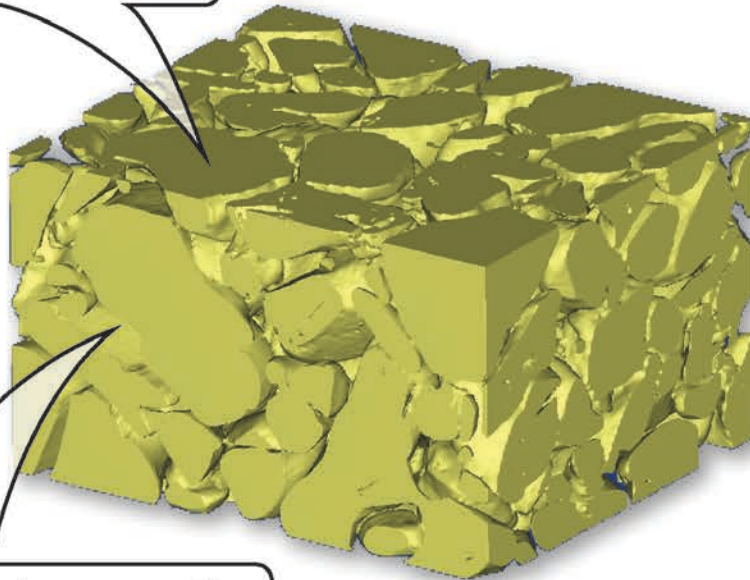
Effective thermal properties can be derived from analysis of the resolved electrode microstructure

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Intrinsic cathode properties

- $\rho_c = 2328 \text{ kg m}^{-3}$
- $c_p = 1269 \text{ J kg}^{-1} \text{ K}^{-1}$
- $k_c = 1.58 \text{ W m}^{-1} \text{ K}^{-1}$



Intrinsic electrolyte properties

- $\rho_e = 1130 \text{ kg m}^{-3}$
- $c_p = 2055 \text{ J kg}^{-1} \text{ K}^{-1}$
- $k_e = 0.60 \text{ W m}^{-1} \text{ K}^{-1}$

Volume average at microscale

$$\rho_{\text{eff}} = \frac{\rho_c V_c + \rho_e V_e}{V_c + V_e}$$

$$c_{p,\text{eff}} = \frac{c_{p,c} V_c + c_{p,e} V_e}{V_c + V_e}$$

Model conduction in composite

$$k_{\text{eff}} = \frac{q''}{L \Delta T}$$

Computed flux q''

Imposed temp. diff. ΔT

Sample thickness L

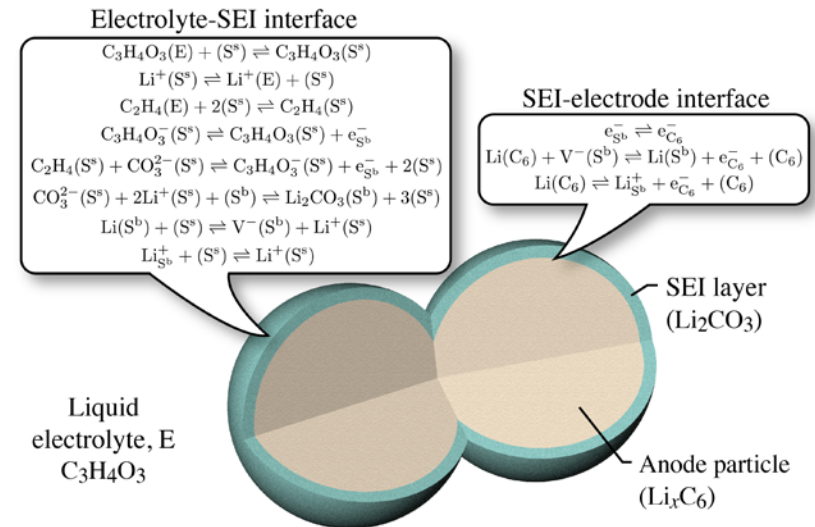
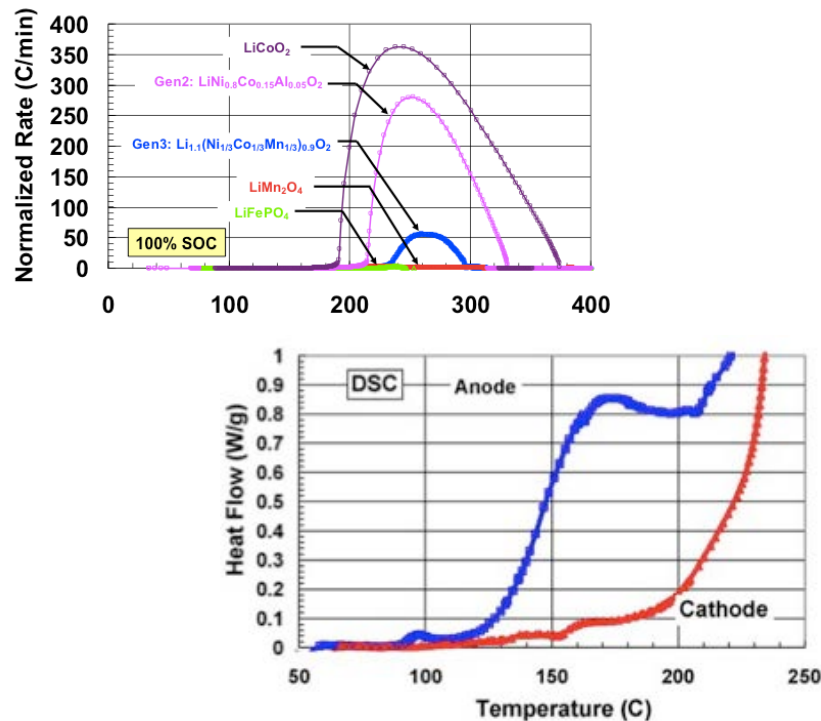
Effective cathode properties

- $\rho_{\text{eff}} = 2006 \text{ kg m}^{-3}$
- $c_{p,\text{eff}} = 1481 \text{ J kg}^{-1} \text{ K}^{-1}$
- $k_{\text{eff}} = 1.19 \text{ W m}^{-1} \text{ K}^{-1}$

- Team:
 - Sandia (prime) – electrochemistry, electrode models, additional physics integration involving thermal runaway
 - Oak Ridge – CAEBAT open architecture, integration.
 - Colorado School of Mines – upscaling (average values and statistical variations)
- Collaboration/project leverage
 - Sandia internal programs on defense-related battery programs.
 - Duracell Crada -> Modeling alkaline batteries in 1,2, and 3D with same software
- Soliciting other groups – facilitated by open source github site:
 - Prof. Tito Busani UNM (EE dept) Li-S battery modeling
 - Reese Jones, Marie Kane, SNL, Li-Air simulations

Remaining Challenges –

Get infrastructure ready for:



- We seek to develop a software platform to model thermal abuse using a speciation and fully reversible-thermodynamics approach.

Proposed future work

FY15

- Implement solid mechanics, partial saturation models, and pressurization models to enable multi-phase capability
- Document upscaling algorithms.
- Integrate SEI models. Demonstrate capabilities. Compare with BATLab data.
Last item is a key project goal: demonstration of flexibility to adopt literature models to address complicated, multi-physics issues within CAEBAT architecture.

LongTerm

- Develop partnerships through open source platforms to create synergistic programs to combine experimental measurements, upscaling of molecular modeling, and software at the cell level to address the development of battery mechanisms.

Response to Reviewer Comments

- This is the first year for this project.

Summary

- We are on schedule to complete the major first year goals. Overcame copyright assertion delays.
- We have integrated the model into the CAEBAT architecture with validation underway. A list of tasks has been generated to complete the validation.
- We have carried out calculations at the pore scale developing an understanding of Joule heating and local stress concentrations, and have developed plans based on heat release look-up tables.

Technical Back-Up Slides

Cantrilbat Electrode Objects

Electrode_CSTR - production

CSTR approximation with surface interfacial Rxn object. Model for intercatated electrode without solid phase diffusion limitation

Electrode_MP_RxnExtent - production

Single Extent Variable with an effective SS diffusion model. Multiple OCV Regions allowed

Electrode_InfCapacity - production

surface interfacial Rxn object with non-varying solid phase

Electrode_MultiPlateau - production

Phase Change Electrode model. Multiple OCV Regions allowed
Effective Diffusion in prep (EAR99, thermal battery)

Electrode_SimplePhaseChangeDiffusion - frozen – to be hardened.

Phase Change Electrode model with diffusional capacitance terms.

Electrode_SimpleDiffusion , Electrode_DiffTALE - **DONE**

Model for intercalated electrode with solid phase diffusion. TALE method handles volumetric expansion and lattice source terms.

Electrode_RadialDiffRegions - initial planning

Expansion of SimpleDiffusion to multiple regions separated by internal interfacial rxns. (SEI) layer

TASK A Implement 1DElectrode capability within CAEBAT and verify.

Task A will focus on porting Sandia's existing Electrode Object and 1D solve capability into CAEBAT open architecture platform. We will perform verification exercises by comparing results against existing capabilities with CAEBAT from the Dualfoil and NTG battery cell modeling capabilities.

A-1 Port Sandia's Electrode Object into CAEBAT

Port Sandia's Electrode Object into CAEBAT open architecture platform, solving issues involved with I/O, and global vs. local coupling strategies.

A-2 Document Implementation of 1D Electrode Object

A-3 Develop Needed Constitutive Models for Verification and coupling between Electrode Object and CAEBAT

A-4 Develop infrastructure for New Electrode Objects Implement Colclasure et al.'s SEI model

A-5 Verify 1DElectrode implementation within CAEBAT Duplicate existing calculations

TASK B Implement partially saturated porous flow and solid mechanics modeling with CAEBAT

Additional physical phenomena will be added to the 1DElectrode model. We will implement a partial saturation porous flow model within the cell model. We will add thermo-electro-mechanical interactions within porous materials that determine the heat, mass and electrical transport processes, addressing cell-level structural evolution under normal operation and abusive conditions..

B-1 Implement partial saturation model for porous flow
Implement models for unsaturated porous flow within the CAEBAT/Electrode architecture.

B-2 Implement solid mechanics within the CAEBAT/Electrode
Implement models for solid mechanics modeling within the . CAEBAT/Electrode architecture using the principles of effective stress to handle the fluid-structure interactions. Linkage with microstructural evolutions will be made.

TASK C Implement upscaling ideas from microstructure models within CAEBAT.

Task C will focus on upscaling the results of microstructure calculations into the macrohomogeneous scale to inform constitutive models.

C-1 Implement the results of upscaling as constitutive models

The first level of upscaling will be to calculate average for key macrohomogeneous parameters.

C-2 Statistical treatments for upscaling

Implement a statistical distribution treatment of results from microstructural transport and chemistry simulations. Abnormal events typically start at locations where local conditions vary from the average conditions leading to temperature or voltage excursions which create abnormal initiation events.

C-3 On-the-fly invocations of microstructural simulations

Extend the OAS framework to handle automatic invocation of detailed simulations at the microstructure level. Upscaling of parameters at the electrode level will lead to improved predictive capability.

TASK D Exercise new capability by implementing thermal runaway models

Task D will focus on demonstrate this new infrastructure with models that will address the thermal runaway process observed to occur within Li-ion batteries. We will start with models proposed in the literature and then couple the suggested mechanisms with correct thermodynamic and transport parameters. We will then evaluate the proposed models using experimental data from Sandia's BATLab program.

D-1 Implement existing engineering models for heat release

D-2 Develop new models for SEI Analogs to corrosion system models will guide our implementation

D-3 Develop models for precombustion processes for the cathode and electrolyte at elevated temperatures

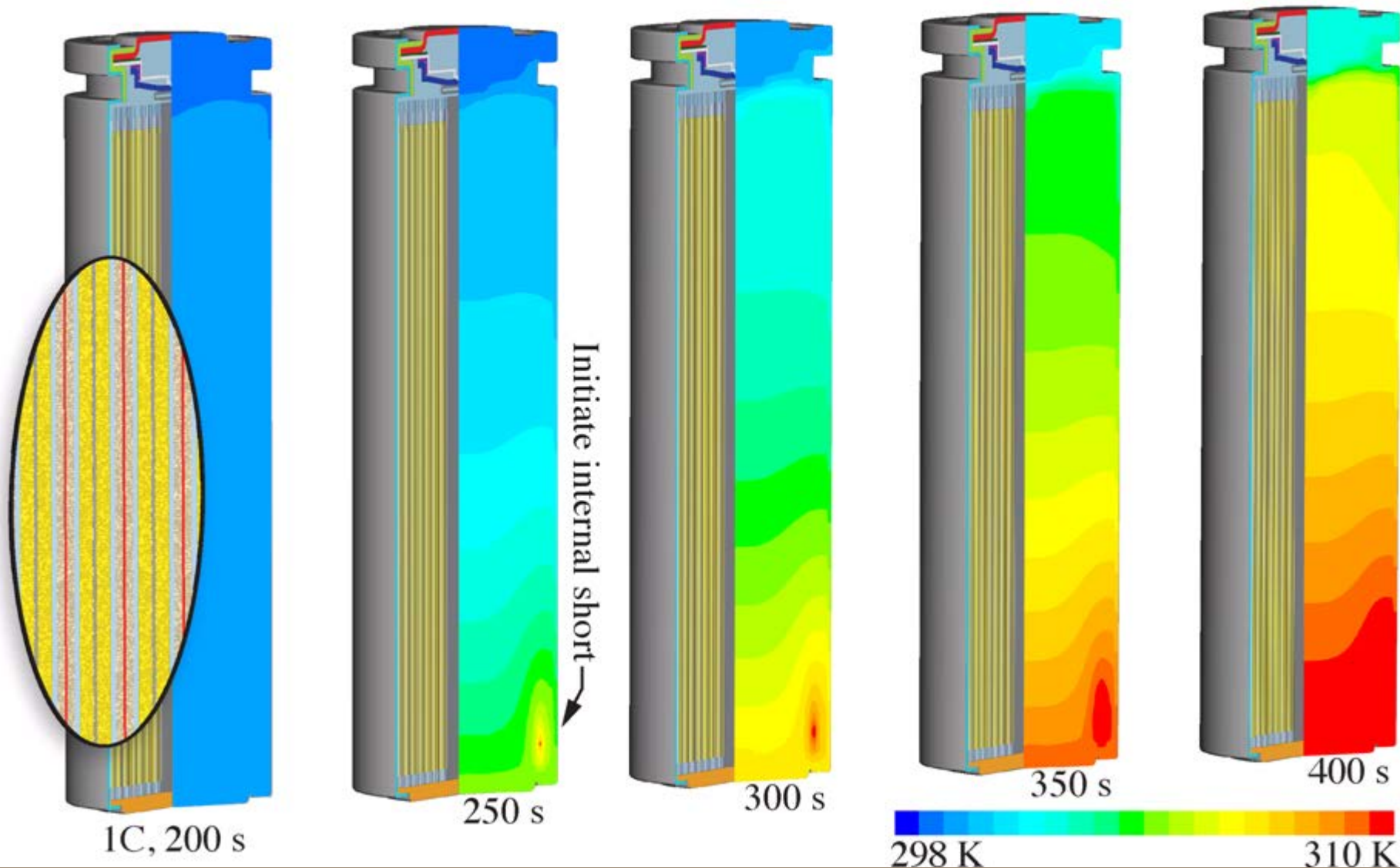
D-4 Fit BATLab data.

Refine models for heat generation due to overheating by comparison to BATLab data. The goal is to successfully develop species dependent models for the autocatalysis mechanism for thermal runaway.

Internal shorts produce locally high heat release, significantly altering the thermal response

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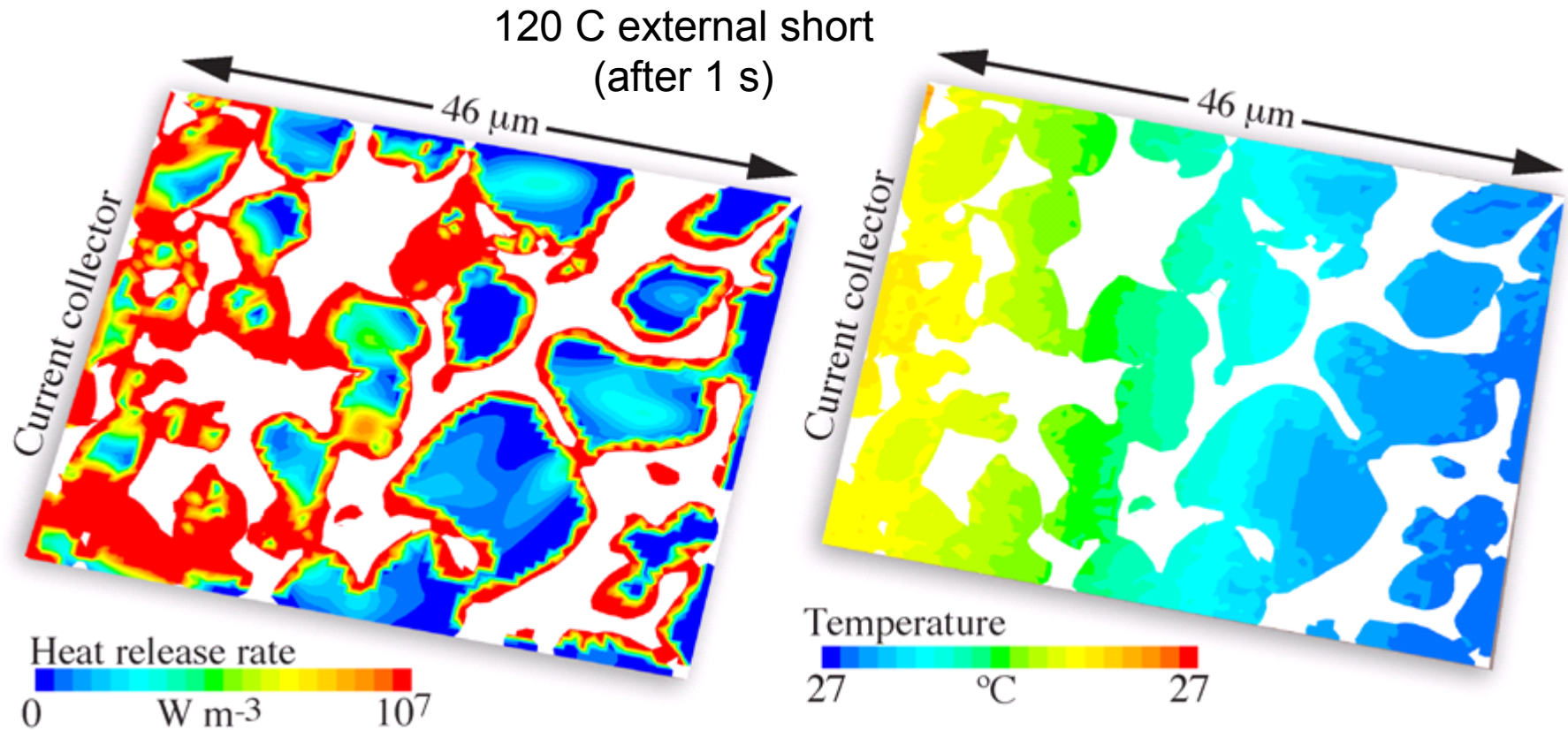
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Temperature variations at the microscale are small, even with very high heat generation rates

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Relatively high conductivity effectively spreads heat over small distances

The cathode charge-transfer chemistry is based on a semi-empirical Butler-Volmer formulation

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Butler-Volmer charge transfer

$$\dot{s}_e = i_o \left[\exp \left(\frac{\alpha_a F \eta_{act}}{RT} \right) - \exp \left(-\frac{\alpha_c F \eta_{act}}{RT} \right) \right]$$

Activation overpotential

$$\eta_{act} = \Phi_{ed} - \Phi_{el} - E^{eq}$$

Equilibrium electric potential difference

$$E^{eq} = E_{ref}^{eq} + \frac{\partial E^{eq}}{\partial T} (T - T_{ref})$$

Exchange current density

$$i_o = k_r F C_{Li^+}^{\alpha_a} [C_{Li}^{max} - C_{Li}]^{\alpha_a} C_{Li}^{\alpha_c}$$

Cathode equilibrium reference potential

$$E_{p,ref}^{eq} = 4.04596 + \exp(-42.30027\theta_p + 16.56714) - 0.04880 \arctan(50.01833\theta_p - 26.48897) - 0.05447 \arctan(18.99678\theta_p - 12.32362) - \exp(78.24095\theta_p - 78.68074)$$

